(2)

OFFICE OF NAVAL RESEARCH

Contract No. N-00014-86-C-0808

Technical Report No. 5

A GENERIC I-BIEM CODE FOR ELECTROCHEMICAL PROBLEMS

by
B.D. Cahan and O. Lafe
To be submitted to the
Journal of the Electrochemical Society

Case Center for Electrochemical Sciences
and the Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106-2699

Subcontract through
The Eveready Battery Company
Westlake, Ohio 44145

15 March 1990

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release: distribution unlimited
2b DECLASSIFICATION / DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 4	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION Chemistry Dept. and Case Center for Electrochemical Sciences 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION Office of Naval Research Chemistry Code 472
6c ADDRESS (City, State, and ZIP Code) Case Western Reserve University Cleveland, OH 44106-2699	7b ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, VA 2217
8a NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N-00014086-C-0808
8c ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
On the Iterative Boundary Element Method

12 PERSONAL AUTHOR(S)
B. D. Cahan and O. Lafe

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Iterim Technical	FROM _____ TO _____	3/15/90	

16 SUPPLEMENTARY NOTATION
Submitted to BETECH 90, July 10-12, 1990, University of Delaware

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

A generalized iterative scheme is developed for the solution of a large class of boundary integral equations. The code is an excellent method for solving problems with huge coefficient matrices The scheme avoids the use of large computer storage spaces and a direct inversion of the matrices is also not required. The result is a considerable improvement over existing boundary integral equation schemes in terms of computer running time and accuracy for problems especially those with complex shapes and boundary conditions.

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert Nowak	22b TELEPHONE (Include Area Code) (202) 696-5075 / 22c OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

A Generic I-BIEM Code for Electrochemical Problems

B.D. Cahan and O. Lafe

Case Center for Electrochemical Sciences

Case Western Reserve University, Cleveland, Ohio 44106.

Abstract

A generic computer code based on the iterative boundary integral equation method (I-BIEM) is developed for simulating a variety of electrochemical problems. In this work we have extended the reach of the method by developing a generalized program capable of solving a wide range of electrodeposition problems. The new code accomodates quite easily multi-variable problems including those with curved boundaries, and non-linear boundary conditions. Such problems include anomalous codeposition of alloys, incorporating the effects of convective and diffusive mass transport; time variant effects such as would be observed in extended growth calculations and pulse plating; microstructural modeling with reference to nonisotropic boundary conditions and crystallographic effects. Some interesting results of real-life simulations are presented.

Introduction

Complex electrochemical processes in domains of nontrivial geometries are generally difficult phenomena to simulate. The advent of the iterative boundary integral equation method, I-BIEM, developed by Cahan *et al* (1988), has made the efficient study of such complicated processes a possibility using a computer of medium memory and storage capability. The flexibility that the method allows, in terms of model refinement at no significant increase in memory or storage requirements, gives this new technique a major advantage over existing codes for studying electrochemical processes.

Convective-diffusion processes are handled efficiently in a way that minimizes numerical discretization errors that commonly pollute the description of the underlying physical process when using other numerical methods.

Since all essential numerical operations are performed solely on the problem boundary, the method is an excellent tool for modeling codeposition and microstructuring. This is because the computed variables are precisely those pertinent boundary quantities required for the solution. The iterative nature of the method makes for an efficient handling of transient phenomena. The dynamic changes in geometry often occurring in electrochemical processes as in the formation of dendrites, nodules and other surfaces including fractals are neatly simulated using the I-BIEM.

Many of these problems are governed by Poisson-type equations rather than the Laplace's equation. In the latter the right hand side is zero whereas we use the term Poisson-like to describe all other problems where the right hand side may be a constant, a known function of position and/or time or a function of the dependent variable itself.

In the development of the new generic code the following steps have been taken:

1. Several practical electrochemical problems are described in terms of fundamental or empirically determined relationships;
2. Appropriate differential and/or integral equations describing the system are selected
3. Algorithmic tools are then developed to incorporating these into I-BIEM.

Description of Key Electrochemical Problems

- Coupled Diffusion-Current Distribution/Anamolous Codeposition
  In many cases simple solution of the current distribution of the problem without consideration of other variables can provide enough information to give deep insights into the underlying principles of a particular problem. (This is often helped by the fact that, for example, diffusion problems have solutions similar although not exactly those of potential distribution problems, at least in small dimensions.) Intermediate scale problems can often be handled by the use of simple "correction terms" based on well recognized engineering principles. In some cases, such as in alloy deposition, this is more often than not the weak point of a treatment.

  In such cases a more rigorous solution involves the simultaneous solution of multiple variables which are interrelated at the boundaries. A rigorous treatment of anomalous deposition, for example, will require simultaneous solution of:

  1. potential-current distribution ;
  2. concentrations of two independent species (Ni and Co) and

3. local pH.

Only (1) can be treated using a straight Laplacian formulation. The others have to be given various levels of sophistication in Poisson-like formulations. For example

- Simple diffusion in a large scale system. Here only the region near the boundary is relevant. Most of the bulk liquid is relatively unaltered by the electrodeposition processes.
- Several of the species, such as Ni and Co, can be treated as independent species connected only by the boundary (kinetics etc.) equations. No cross terms in the bulk need be considered. If the pH is a relevant variable and/or the precipitation of films occurs at the interface cross terms for the bulk must now be considered.

- Composition Variation
  Since the boundary equations are different for each of the sub fields discussed above, the problem of lateral variability of such deposits is not necessarily obvious. When compositional variation in the thickness of the media is important this must be treated by developing the time dependent solutions of the sets of equations described above.

- Microstructural Models
  To date I-BIEM has been used primarily for macroscopic modeling studies. Since the same fundamental governing equations apply in the micro scale with the exception that stochastic variation in local parameters must be considered. In addition the properties of the deposit including crystallographic orientations, the development of grain boundaries and the effects of localized segregations in the bulk and at the grain boundaries must be considered.

- Induced Codeposition
  The problem in above is further complicated when minority species are to be considered. Here the local chemistry and/or physics of the situation must be incorporated into the boundary equations.

- Extended Growth
  The mathematical formulation has been shown to be stable even in the presence of physically unstable conditions. The local effects of real surface roughness, impurity inclusions and other similar problems can be treated as extensions of the above. From a fundamental point of view as well as a practical concern the interaction of the relevant variables is interesting. Such studies could for example lead to a better understanding of the formation of nodules, dendrites or other irregularities in printed circuit fabrication.

- Complex Geometries
  Up until now primary emphasis in the development of the I-BIEM has been placed on the mathematical and the algorithmic portions of the code. In order to make the system more "user friendly" and thus applicable to a broad range of problems it was desirable to develop a menu driven method of readily entering or altering boundary geometries and governing equations.

- Current Thieves and Auxiliary Anodes
  This problem is readily handleable once the problem of assignment of complex geometries is solved.

- Stresses in Films/Convective Transport
  Stresses in films are often a consequence of sub processes like hydrogen codeposition in electrodeposited films. In such films the bi-harmonic equation can be used to treat these effects. The bi-harmonic equation should be solvable in terms of the equivalent set of simultaneous Laplace and Poisson equations. These same equations could be used to study the vorticity inherent in the convective transport in plating baths caused by rotation of the disk.

Governing Differential/Integral Equations

Preamble

The class of problems outlined above are generally governed by linear second order partial differential equations of the Poisson-type. The material coefficients involved in some of the cases are functions of the space coordinate (heterogeneity). For such problems the governing equation can be cast, using parameter perturbation technique in a form that is well amenable to treatment by the I-BIEM. The result will be series of Poisson equations the solution of each of which represents identifiable components of the material inhomogeneity.

There are a number of approaches for treating terms involving time derivatives in transient problems:

1. The most direct approach is the use of special time-dependent fundamental solutions in the integral equations for the I-BIEM code. Such solutions are different from the usual logarithmic solutions used in integral equations derived for straight Poisson-type equations. However the use of such complex fundamental equations call for equally tedious implementation of numerical integrations in the computer program.

2. The unsteady governing equations can be transformed so that time is in effect integrated out. A suitable transformation is the Laplace transform method. This will convert the partial differential equation into a Hemholtz-type of equation. The fundamental solution in this case is in the form of a Bessel function. The main challenge in this approach is the inverse transformation back to the physical time domain. There exist in the literature a number of efficient numerical algorithm (e.g. Schapery 1962, Bellman em et al 1966, Stehfest 1970) for performing the inverse transformation.

3. The terms involving time derivatives are replaced by their equivalent finite differences. The resulting equations are either of the Poisson or Helmholtz type and the numerical process will necessarily involve performing area/domain integrations in addition to the calculations carried out on the boundary.

Mathematical Formulation

- *Differential Equations*
  Consider an electrochemical domain Ω consisting of the boundary Γ. In general the process can be described by the differential equation:

$$\nabla^2\phi(\mathbf{x},t) = \mathcal{F}(\phi, \frac{\partial\phi}{\partial t}, \mathbf{x}, t) \tag{1}$$

where ∇^2 is the Laplacian operator in space ($\mathbf{x}$), t is time, ϕ can represent voltage (V), concentration (c) or temperature (T) while $\mathcal{F}$ represents some forcing functions which takes on the following forms depending on the character of the problem:

- Diffusion Problems $\phi \Rightarrow c$

$$\mathcal{F} = D\frac{\partial c}{\partial t}$$

where D is the diffusion coefficient. In that case eqn(1) when transformed into the Laplace domain takes on the form:

$$\nabla^2 \bar{c} - \beta^2(\bar{c} - c_{t=0}) = 0$$

in which $\beta = \sqrt{sD}$, s is the transform parameter and $\bar{c} = \int_0^\infty c \exp(-st)\, dt$.

- Convective Problems

$$\mathcal{F} = -\underline{v} \cdot \nabla\phi$$

where $\underline{v}$ is the velocity.

- Heat Production (Sources & Sinks)

$$\mathcal{F}(\mathbf{x}) = \sum_i f_i\, \delta(\mathbf{x}, \mathbf{x}')$$

where δ is the Dirac delta function while f_i represents the strength of the i-the source or sink.

- Non-linear Problems

$$\mathcal{F} = \mathcal{F}(\phi)$$

The conditions associated with the boundary Γ can in general be written in the form:

$$\sigma\mathcal{D}[\phi(\mathbf{x})] + f(\phi, \mathbf{x}) = 0 \tag{2}$$

where $\mathcal{D}$ is a differential operator, σ is a coefficient and f is some prescribed function of ϕ On a conductor $\sigma = 0$ while on an insulator $f \equiv 0$.

- *Integral Equations*

The first task in a BIEM process is to convert the governing partial differential eqn(1) into a suitable integral equation. This is achieved by multiplying the equation by a function g, integrating the ensuing expression over Ω and invoking the Green's identities. The result of such manipulations is the integral equation:

$$\alpha\phi(\mathbf{x}) = \int_\Gamma \{\phi(\mathbf{x}')\frac{\partial g}{\partial n}(\mathbf{x}, \mathbf{x}') - g(\mathbf{x}, \mathbf{x}')\frac{\partial \phi}{\partial n}(\mathbf{x}')\}\, d\Gamma(\mathbf{x}') + \int_\Omega g(\mathbf{x}, \mathbf{x}'')\mathcal{F}(\mathbf{x}'')\, d\Omega(\mathbf{x}'') \tag{3}$$

where n is along the unit outward normal to the boundary and α is the Cauchy principal value of the integration of the Green's function singularity since the following equation is to be satisfied by g:

$$\mathcal{L}[g(\mathbf{x}, \mathbf{x}')] = \delta(\mathbf{x}, \mathbf{x}') \tag{4}$$

where $\mathcal{L} = \nabla^2$ for Poisson-type problems and $\mathcal{L} = \nabla^2 - \beta^2$ for Helmholtz-types.

I-BIEM

Coefficient Matrices

To use the boundary integral equation method the boundary Γ is subdivided into a finite number of elements and suitable interpolation functions are chosen to represent the distribution of the dependent variables on the boundary. For function ϕ on Γ we write:

$$\phi(\mathbf{x}) = \sum_i N_i(\mathbf{x})\phi_i \tag{5}$$

where ϕ_i are the values of ϕ at the discrete points on the boundary and N_i are shape functions. A similar expression can be written for $\partial\phi/\partial n$. To perform boundary integrations we select a finite number of points to serve as integration origins ($\mathbf{x}$ in eqn 3). In most BIEM implementations these points are located along the boundary segments and usually fall on the nodes formed at element intersections. In a few implementations (the so-called non-singular formulation) the integration points are selected outside Ω. In I-BIEM $\mathbf{x}$ can be placed on Γ, inside or outside of Ω. The number of independent integration points selected is the same as the number, M, of unknown ϕ and $\phi_n = \partial\phi/\partial n$ on the boundary.

When these integrations are performed eqn(3) becomes:

$$\xi_i = \sum_{j=1}^{M} a_{ij}\phi_j - \sum_{j=1}^{M} b_{ij}\phi_{n_j} + c_i \quad i = 1, 2, \cdots, M \tag{6}$$

where

$$\begin{aligned}
\xi_i &= \alpha\phi(\mathbf{x}_i) \\
a_{ij} &= \int_{\Gamma_j} g(\mathbf{x}, \mathbf{x}') \frac{\partial N_i}{\partial n}(\mathbf{x}')\, d\Gamma \\
b_{ij} &= \int_{\Gamma_j} \frac{\partial g}{\partial n}(\mathbf{x}, \mathbf{x}') N_i(\mathbf{x}')\, d\Gamma \\
c_i &= \int_{\Omega} g(\mathbf{x}, \mathbf{x}'') f(\mathbf{x}'')\, d\Omega(\mathbf{x}'')
\end{aligned}$$

When the integration points $\mathbf{x}_i$ fall outside Ω then $\xi_i \equiv 0$.

To solve for the unknown ϕ and ϕ_n at the nodes we start by guessing any initial values, ϕ^e and ϕ_n^e for these quantities. On a conductor (exact ϕ^e) or on an insulator (exact ϕ_n^e) type problems the known quantities can be used once and for all in eqn(6) and the results absolved into the coefficients c_i. For linear mixed boundary conditions one will normally eliminate either ϕ or ϕ_n for the other. In non-linear mixed conditions the iterative process readily accepts the incorporation of any root-finding routine in the solution process as will become clear shortly. When the guesses are used in the equation written for the i-th node as origin of integration (see eqn 6) the result is an error:

$$\varepsilon_i = \sum_{j=1}^{M} a_{ij}\phi_j^e - \sum_{j=1}^{M} b_{ij}\phi_{n_j}^e + c_i \tag{7}$$

We then update the guesses by assuming on:

- Flux Boundaries (e.g. Insulators)

$$\phi_i = \phi_i^e + \lambda \frac{\varepsilon_i}{a_{ii}} \tag{8}$$

- Dirichlet Boundaries (e.g. Conductors)

$$\phi_{n_i} = \phi_{n_i}^e - \lambda \frac{\varepsilon_i}{b_{ii}} \tag{9}$$

- Mixed Boundaries (e.g. Tafel)

$$a_{ii}(\phi_i - \phi_i^e) - b_{ii}(\phi_{n_i} - \phi_{n_i}^e) = \lambda \varepsilon_i \tag{10}$$

where λ is in an over-relaxation factor. For a segment with a mixed boundary condition eqn(10) is to be solved with the relevant prescribed condition as shown by eqn(2).

The above process is repeated for all points until a suitable convergence criterion is satisfied.

Capabilities of the Developed I-BIEM Code

- *Poisson Equations*
  The code handles the solution of Poisson-type equations. This permits the evaluation of the effect of diffusion convection and time varying problems. Problems other than these mentioned above which could be tackled with this module would include:

  Pulse plating;
  - Magnetic fields including detailed modeling of recording heads;
  - Sources and sinks as might be found in problems associated with internally generated thermal fluxes.

- *Tesselation*
  In order to deal with problems governed by Poisson-type equations it was necessary to develop a generalized and optimizeable scheme for subdivision of the domain (however complex) into readily integrable subdomains. This has been devised to require a minimal intervention from the user's point of view.

- *Generalized Boundary Input*
  Automatic definition of the position and subdivision of the boundaries for particular problems. Provides a generalized CAD-like data input approach for a wide variety of problems.

Examples

Conclusions

References

1. Abramowitz, M. and I.A. Stegun, **Handbook of Mathematical Functions**, National Bureaux of Standards Applied Math. Series (55), 1964.